Journal of South American Earth Sciences 33 (2012) 1–7

Contents lists available at ScienceDirect

Journal of South American Earth Sciences

journal homepage: www.elsevier.com/locate/jsames

A 2400-year record of trace metal loading in lake sediments of Lagoa Vermelha, southeastern Brazil

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ARTICLE INFO

Article history:
Received 7 December 2010
Accepted 25 July 2011

Keywords:
Lake sediments
Metals
Pb stable isotopes
Atmospheric fallout

ABSTRACT

Sediments of the Lagoa Vermelha (Red Lake), situated in the Ribeira Valley, southeastern Brazil, are made of a homogeneous, organic-rich, black clay with no visible sedimentary structures. The inorganic geochemical record (Al, As, Ba, Br, Co,Cs, Cr, Fe, Mn, Ni, Rb, Sc, Sb, V, Zn, Hg and Pb) of the lake sediments was analyzed in a core spanning 2430 years. The largest temporal changes in trace metal contents occurred approximately within the last 180 years. Recent sediments were found to be enriched in Pb, Zn, Hg, Ni, Mn, Br and Sb (more than 2-fold increase with respect to the "natural background level"). The enhanced accumulation of Br, Sb, and Mn was attributed to biogeochemical processes and diagenesis. On the other hand, the anomalous concentrations of Pb, Zn, Hg and Ni were attributed to pollution. As Lagoa Vermelha is located in a relatively pristine area, far removed from direct contamination sources, the increased metal contents of surface sediments most likely resulted from atmospheric fallout. Stable Pb isotopes provided additional evidence for anthropogenic contamination. The shift of ^{206}Pb/^{207}Pb ratios toward decreasing values in the increasingly younger sediments is consistent with an increasing contribution of airborne anthropogenic lead. In the uppermost sediments (0–10 cm), the lowest values of the ^{206}Pb/^{207}Pb ratios may reflect the influence of the less radiogenic Pb from the Ribeira Valley District ores (^{206}Pb/^{207}Pb between 1.04 and 1.10), emitted during the last 50 years.

1. Introduction

Lake sediments are relatively closed systems that provide long-term records of past environmental conditions. Analyses of metals in lacustrine sediments have thus been used to reconstruct temporal variations of natural and anthropogenic inputs into the lake ecosystem (Dabous, 2002; Yang et al., 2003; Lepane et al., 2007; Wu et al., 2007; Karageorgis et al., 2009; Wang et al., 2010). In general, enrichment of metals in surface sediments has been attributed to human activity, and in remote areas the most probable source is atmospheric transported contaminants. However, post depositional processes can also affect the distribution of metals in lake profiles, and must therefore be considered in the interpretation of the pollution trends (El Bilali et al., 2002; Outridge et al., 2005).

Anthropogenic emissions increased drastically from the beginning of the 20th century, mainly from fuel combustion, smelting and refuse incineration (Nriagu, 1996). In the Northern Hemisphere, airborne metal pollution has been registered in various types of natural deposits, especially the polar ice caps (Rosman et al., 1997; Van der Velde et al., 2000), ombrogenic bogs (Shotyk et al., 2001, 2005; Roos-Barraclough et al., 2002) and aquatic sediments (Von Gunten et al., 1997; Camarero et al., 2009; Shuchun et al., 2009; Michellutti et al., 2009; Yang et al., 2010). In the Southern Hemisphere, only a few studies have been done on airborne metal pollution (Nriagu et al., 1996; Biester et al., 2002; Planchon et al., 2002; Pearson et al., 2010), and among the most important are those aiming to reconstruct the history of metal pollution in the South American Andes (Abbot and Wolfe, 2003; Cooke et al., 2007, 2008, 2009a,b) where mining and metallurgical activities date as far back as 1400 years BC.

This study examines the vertical distribution of trace elements As, Ba, Br, Co,Cs, Cr, Ni, Rb, Sc, Sb, V, Zn, Hg and Pb, and major elements such as Al, Fe and Mn in the sediments of a small lake — Lagoa Vermelha (Red Lake) — located in a protected area of the

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doi:10.1016/j.jsames.2011.07.007

Upper Ribeira State Park, in the Ribeira Valley, southeastern Brazil. Although situated in an undisturbed catchment, remote from direct human impacts, the lake is close to areas that have been sites of numerous mining (Pb–Zn–Ag) and smelter activities from 1945 to the end of the 20th century (Moraes et al., 2004). Thus, Lagoa Vermelha is a good target for recording atmospheric pollution originating from the mines. Furthermore, remote sources such as leaded gasoline and emissions from industrial sectors could have also contributed to the metal burden of the sediments. Here we aim to assess the possible influx of anthropogenic metals to the lake sediments, and to make inferences about possible sources of lead, using lead isotopes (Outridge et al., 2002; Renberg et al., 2002; Couillard et al., 2008; Hosono et al., 2010).

2. Methods

2.1. Study site

(Fig. 1) Lagoa Vermelha (24°23′18″S, 48°31′44″W) is a small mountain lake roughly elliptical (70 × 100 m), with a maximum depth of 5 m, situated in the Atlantic Plateau region, 500 m above sea level and 100 km inland from the southeastern Atlantic coastline. The area is covered by dense tropical vegetation which is a remnant of the tropical Brazilian rainforest known as the Mata Atlantica. The predominant soils in the region are classified as *dystropept*, according to American Soil Taxonomy, USDA classification (Soil Survey Staff, 1999). Meteorological data indicate mean winter and summer temperatures of 14 and 27 °C, respectively, and mean annual rainfall of 1600 mm (Karmann et al., 2007).

The catchment rocks consist mainly of limestones mixed with metasiltites and phyllites of the Late Proterozoic Açungui Group (Campanha and Sadowski, 1999). The metasedimentary rocks of the Açungui Group are host to many Pb–Zn–Ag deposits that belong to the Ribeira Valley Lead District. The most common sulfide minerals are galena, sphalerite, chalcopyrite, pyrite and tennantite-tetrahedrite (Daitx, 1996).

2.2. Sampling

A 290-cm long undisturbed core was obtained from the lake using a vibracorer device and a 7.6-cm diameter aluminum tube (Martin et al., 1995). The core was maintained vertically and kept cool during transportation. In the laboratory, the tube was opened, the sediment macroscopically described, and sliced at 5 cm from the surface to the bottom. Twenty bulk samples were selected throughout the core for the present study.

2.3. Analytical procedures

Oven dried samples at 60 °C for 24 h were finely ground with a tungsten mill.

Al, Fe and Mn were determined by wavelength-dispersive X-ray fluorescence spectroscopy (XRF) using fused glass discs. The precision of these measurements was better than 5% RSD. Loss on ignition (LOI) was determined from dry samples at 530 °C.

As, Br, Ba, Co, Cr, Cs, Ni, Rb, Sc, Sb, V, and Zn were analyzed using instrumental neutron activation (INAA) Samples reference materials and synthetic standards were irradiated for 16 h, in a thermal neutron flux of 10^{12} n cm^{-1}s^{-1} in the IEA-R1 nuclear reactor at IPEN–Institute of Nuclear and Energetic Research (São Paulo). The INAA and AAS methodologies were validated by assays of reference materials NIST SRM 8704, Soil 7 – IAEA, BEN (Basalt–IWG-GIT), and NIST SRM 2704, NIST SRM 1646, BCR CRM 280, respectively.

Mercury was determined separately by cold vapor-atomic absorption spectrometry (CV-AAS) technique in a flow injection mercury system (FIMS-Perkin Elmer), after total digestion in a mixture of HNO_3, H_2SO_4 and H_2O_2. All Hg determinations were performed in duplicate, and the results agreed to within 10%. The lower limit detection for the elements determined by XRF, INAA and AAS were well below the lowest measured concentrations in all samples.

For the determination of Pb isotope ratios, samples were dissolved with a mixture of HF, HNO_3 and HCl acids in PARR® bombs. The solutions were dried, converted to HBr 0.7 M and the Pb was purified using a standard ion exchange technique; Pb was eluted

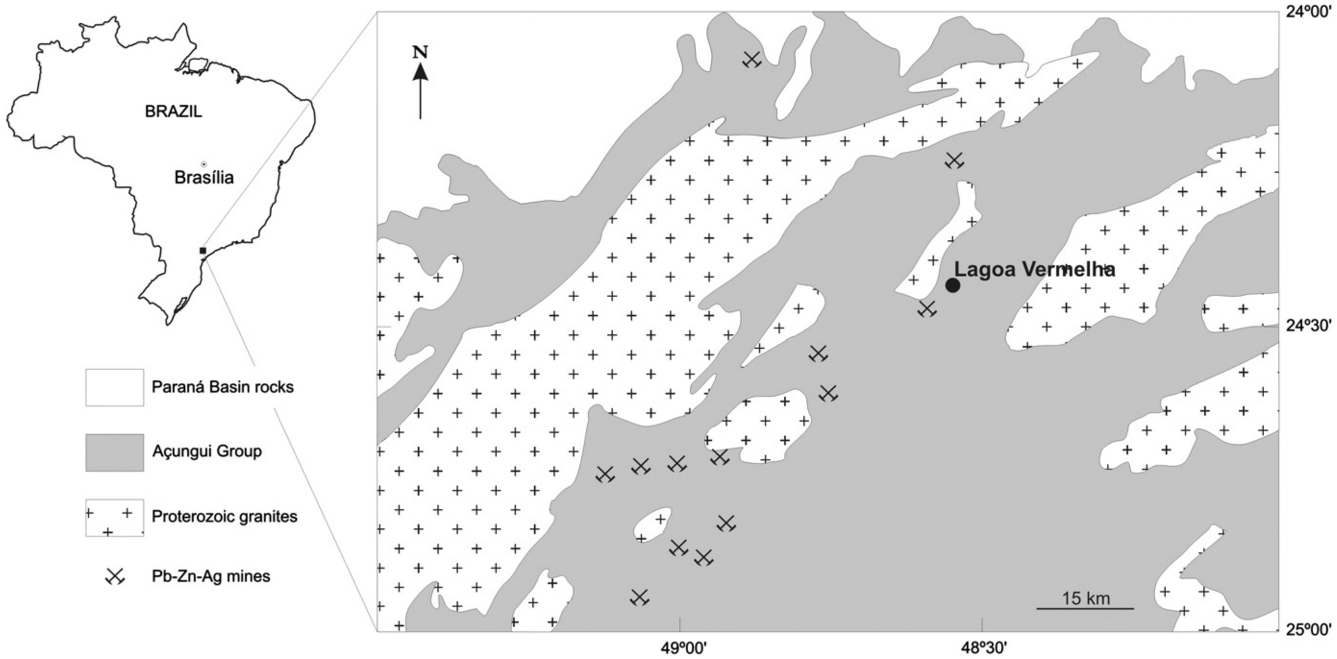

Fig. 1. Location map of Lagoa Vermelha. Main geological units and ancient mining operations (simplified from Daitx, 1996).

with HCl 6 M. Pb concentrations were determined by the ID-TIMS technique using a ^{208}Pb-enriched spike. The Pb isotopic ratios were measured using a VG 354 multicollector mass spectrometer. Mass fractionation was determined based on multiple analyses of the NBS-981 Common Pb standard. Total Pb analytical blanks were lower than 150 pg and had a negligible effect on the isotopic ratios. Pb analysis accuracy is given by multiple runs ($n = 7$) on the USGS Standard Material BCR-1 (Woodhead and Hergt, 1999) which yielded a Pb concentration of 13.127 ± 0.27 and ^{206}Pb/^{204}Pb = 18.745 ± 0.012, ^{207}Pb/^{204}Pb = 15.631 ± 0.029, ^{208}Pb/^{204}Pb = 38.653 ± 0.090. All analyses were performed at the Center of Geochronological Research at the University of São Paulo.

Five samples were ^{14}C dated by accelerator mass spectrometry at the Isotrace Laboratory, University of Toronto.

3. Results and discussion

3.1. Sediment description and dating

Sediments throughout the depth profile consisted of a homogeneous, organic-rich, black clay with no visible sedimentary structures.

Radiocarbon calibrated dates obtained at different depths are as follows (Fig. 2): 15–20 cm (modern); 100–105 cm (621 ± 71 cal yr. BP); 155–160 cm (1366 ± 76 cal yr. BP); 165–170 cm (1376 ± 71 cal yr. BP); 190–195 cm (1522 ± 109 cal yr. BP); 260–265 cm (2418 ± 125 cal yr. BP).

From the results of the radiocarbon analysis, the average sediment accumulation rate calculated over the upper 105 cm (last 620 years) is 0.169 cm yr^{-1}. For the lower portions of the core, the calculated average sediment accumulation rates are 0.088 cm yr^{-1}, 0.156 cm yr^{-1}, and 0.078 cm yr^{-1} for the 105–170 cm (620–1360 cal yr. BP), 170–195 cm (1360–1520 cal yr. BP), and 195–265 cm (1520–2415 cal yr. BP), respectively.

The geochronological framework indicates that the upper 30 cm of the core reflects the industrial period, corresponding approximately to the last 180 years. The extrapolation of the data sequence provides an age of about 2430 cal yr BP for the sediments at the bottom of the core, at 285 cm depth.

3.2. Trace element concentrations, normalized concentrations, and enrichment factors

Al and Fe concentrations show moderate variations with depth (2.24–4.60% and 1.01–2.00%, respectively), but whereas Al concentrations decrease toward the surface, the behavior of Fe is less regular, with maximum values found in the intermediate depths. Mn (103–296 ppm) shows a profile typical of an oxic sedimentary environment, with increasing concentrations toward the top. The organic matter contents, estimated by LOI concentrations (Heiri et al., 2001), increase gradually from 65.10% at the bottom of the core to 89.42% at the top.

Most trace element profiles show a moderate range of variation throughout the core (As: 4.4–10.9 ppm; Ba: 53–277 ppm; Co: 3.1–8.0 ppm; Cr: 10.6–57.4 ppm; Cs: 0.9–4.1 ppm; Ni: 15.0–32.1 ppm; Rb: 4–45 ppm; V: 15.0–49.8 ppm), and declining patterns toward the surface. Zinc (39.6–85.9 ppm), Br (36.2–81.1 ppm), Hg (38.2–102.4 ppb) and Pb (7.7–18.7 ppm) profiles are more erratic.

Factor analysis with varimax rotation was carried out for organic-free element concentrations, in order to explore element associations and possible common geochemical controls. Two factors, F1 and F2, were extracted from 17 elements, accounting for 54.5% and 27.9% of the total variance, respectively. In the F1 versus F2 plot (Fig. 3), two groups of elements can be distinguished: Ba, Cr, Rb, Cs, Al and Sc with negative loading values in both factors, and Pb, Hg, Ni, Sb, Mn, Br, Zn, Fe, and As with positive loading values in both factors. The first group includes typical geogenic elements, representing material transported into the lake from local geological sources by weathering and erosion. The second group consists of metals, metalloids and Br, which are elements generally associated with the organic fraction of the sediments.

In order to compensate for variations due to differences in the organic fraction in the sediments, element concentrations were normalized to Sc, a refractory lithophile element (Weiss et al., 1999; Shotyk et al., 2001). Fig. 4 displays X/Sc plotted versus depth. Most metals show similar patterns, with a fairly constant baseline at depth, and maximum values near the surface. Anomalous concentrations prevailing only over the last 180 years (0–30 cm), corresponding to the industrial period, can be an indication of anthropogenic input.

A more appropriate way to assess contamination is to take into account enrichment factors (EFs) with respect to a backgroung pre-industrial level. The EFs were calculated as:

$$EF = \Big[(X/Sc)_{\mathrm{sample}}\Big[\Big((X/Sc)_{\mathrm{background}}\Big)\Big],$$

where [(X/Sc)$_{\mathrm{sample}}$] is the ratio of concentration of any element to the concentration of Sc in the sample at a given depth, and [(X/Sc)$_{\mathrm{background}}$] is the ratio of the average concentration of any element to the average concentration of Sc in the in sediments prior to 1830 AD, represented by the 30–285 cm segment of the core.

Results of EF calculations in the 0–30 cm sediments are shown in Fig. 5. EF values around or below 1.0 are observed for the

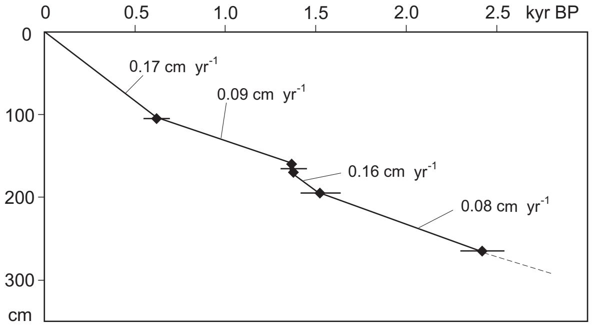

Fig. 2. ^{14}C age depth model for Lagoa Vermelha sediments.

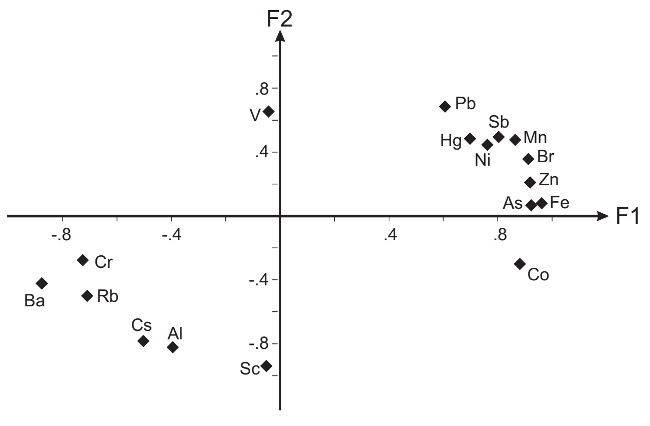

Fig. 3. Biplot of factor analysis: Factor 1 versus factor 2.

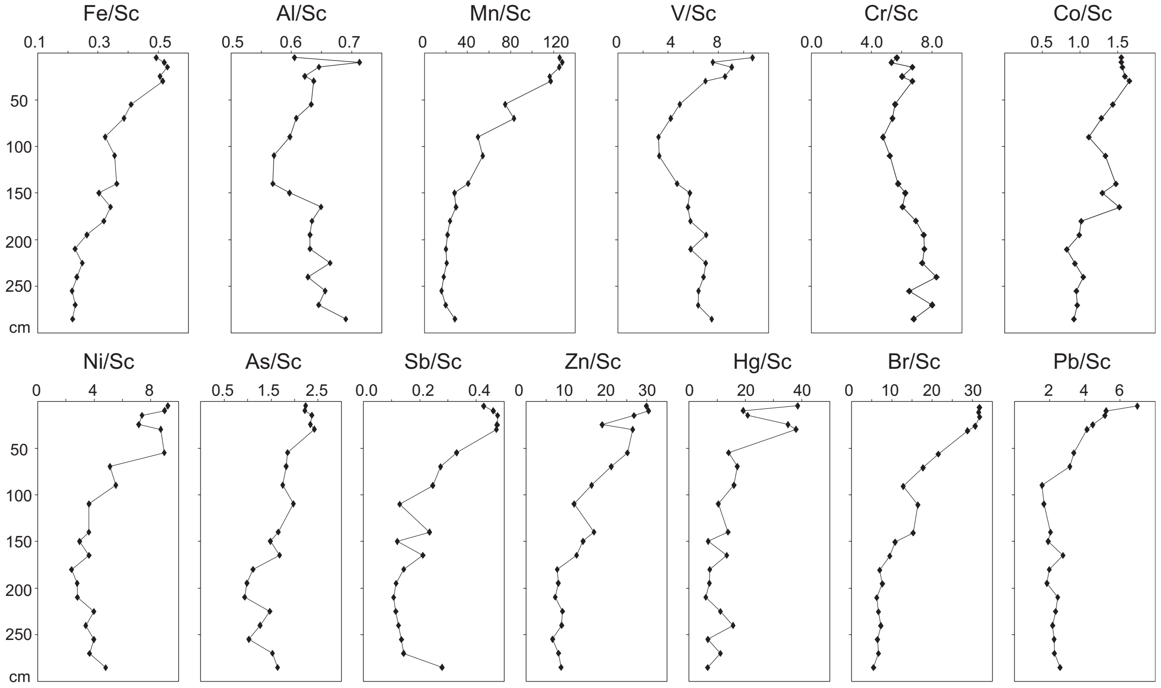

Fig. 4. Sc-normalized concentrations of Fe, Al, Mn, V, Cr, Co, Ni, As, Sb, Zn, Hg, Br and Pb versus depth for the Lagoa Vermelha sediments.

geogenic elements - Al, Cr, Ba, Cs, Rb, confirming their origin from the catchment erosion. Fe, V, As and Co are slightly enriched by a factor of 1.2–1.9. The trace elements Pb, Zn, Hg, Ni, Sb, Mn, Br, display EF values above 2.0, which means contamination inputs and/or significant redistribution due to biogeochemical and diagenetic processes. Manganese is generally concentrated at the surface in sedimentary columns by dissolution at depths under more reducing conditions and reprecipitation under more oxic conditions (Mahler et al., 2006). The anomalous concentrations of Br and Sb could be attributed to their strong affinity for organic matter (Ng and King, 2004; Li et al., 2007; Reimann et al., 2007), which is supplied to the sediments both from the catchment area and the productivity of the lake itself.

On the other hand, the surface enrichment of Hg ($EF_{0-30\ cm} = 1.8-3.5$), Pb ($EF_{0-30\ cm} = 1.8-3.1$), Zn ($EF_{0-30\ cm} = 1.6-2.5$) and Ni ($EF_{0-30\ cm} = 1.8-2.3$) can be assumed to record metal pollution during the industrial period. Since Lagoa Vermelha is located in a rather isolated basin, not subject to point source loadings, the contamination inputs entered the lake most likely via atmospheric deposition. In fact, Hg, Pb, Zn and Ni are commonly emitted to the atmosphere by industrial activities (Nriagu, 1990; Pacyna and Pacyna, 2001). Hg, particularly, is a global pollutant with a long residence time in the atmosphere (1–4 years), and a high potential for long-range transport (Biester et al., 2007). Indeed, with the onset of industrialization (1850 AD) the contribution of airborne anthropogenic Hg increased substantially in the different archives of atmospheric deposition (Perry et al., 2005). In the industrialized region of southern Brazil, many studies consistently show increasing metal concentrations in surface sediments of lakes or marshes situated in regions far from direct pollution sources. For instance, in the Itatiaia mountains in the state of Rio de Janeiro, a study on Pb and Hg in sediments from an ombrothrophic lake indicated that present accumulation rates (Pb = 40–80 mg m^{-2} yr^{-1}; Hg = 15–30 μg m^{-2} yr^{-1}) reflect emissions from industrial sources (Lacerda and Ribeiro, 2004). In Ilha Grande (Great Island), zinc enrichment in the top layers of marsh sediments (rate of deposition = 24–78 mg m^{-2} yr^{-1}) was also attributed to atmospheric deposition (Silva-Filho et al., 1998). Estimates of Pb, Mn and P concentrations in atmospheric suspended particulate matter sampled at Ilha Grande are in the range of typical values for urban areas (Nascimento et al., 2011). Data on Hg flux through litterfall in a primary rainforest at Ilha Grande showed that the canopy efficiently contributes to the input of atmospheric Hg to the soils (Silva-Filho et al., 2006). The potential sources of such metals to the pristine environment of Ilha Grande are believed to be the urban and industrial emissions from the states of São Paulo and Rio de Janeiro. This conclusion is likely to apply to Lagoa Vermelha which is also situated within the boundaries of the industrialized southeastern Brazil. In the Lagoa Vermelha area, however, there is an additional emission source supplied by the metallic aerosols originating from the smelter activities of the Pb–Zn–Ag Ribeira Valley mining district. The significant positive correlation coefficient between concentrations of Zn and Pb in surface sediments ($r^2 = 0.58$) is consistent with their origin from this common source.

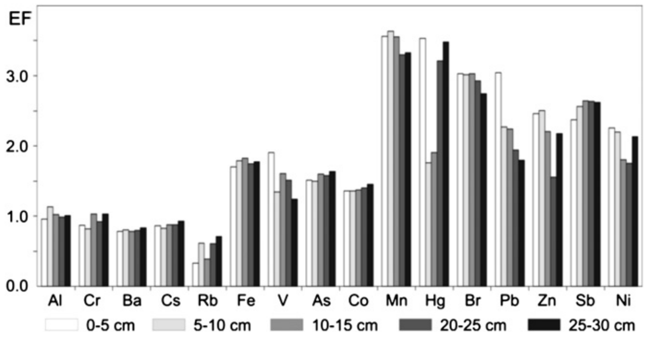

Fig. 5. Enrichment factors estimated for Al, Cr, Ba, Cs, Rb, Fe, V, As, Co, Mn, Hg, Br, Pb, Zn, Sb and Ni in the 0–5, 5–10, 10–15, 20–25 and 25–30 cm sediments, in relation to the "natural background level".

Table 1
Pb isotopic ratios of Lagoa Vermelha sediments.

cm	$^{206}Pb/^{204}Pb$	σ	$^{207}Pb/^{204}Pb$	σ	$^{208}Pb/^{204}Pb$	σ	$^{208}Pb/^{206}Pb$	σ	$^{206}Pb/^{207}Pb$	σ
0–5	20.179	0.008	15.788	0.008	38.071	0.008	1.887	0.001	1.278	0.001
5–10	20.856	0.005	15.857	0.005	37.963	0.005	1.820	0.002	1.315	0.001
10–15	21.035	0.005	15.892	0.004	38.050	0.004	1.809	0.001	1.324	0.001
20–25	21.624	0.006	15.934	0.006	38.104	0.006	1.762	0.001	1.357	0.001
25–30	22.091	0.160	15.977	0.013	38.194	0.013	1.729	0.011	1.383	0.012
50–55	23.696	0.007	16.122	0.006	38.299	0.007	1.616	0.001	1.470	0.001
65–70	23.505	0.005	16.108	0.005	38.350	0.004	1.632	0.001	1.459	0.001
85–90	23.533	0.007	16.118	0.007	38.339	0.007	1.629	0.001	1.460	0.001
105–110	24.006	0.014	16.130	0.013	38.274	0.013	1.595	0.002	1.488	0.003
135–140	24.104	0.010	16.138	0.009	38.302	0.009	1.589	0.001	1.494	0.001
145–150	23.921	0.011	16.147	0.012	38.425	0.012	1.606	0.001	1.481	0.002
160–165	23.013	0.005	16.067	0.006	38.565	0.006	1.676	0.001	1.432	0.002
175–180	24.066	0.011	16.167	0.012	38.558	0.012	1.602	0.001	1.489	0.001
190–195	23.751	0.006	16.138	0.006	38.615	0.006	1.626	0.001	1.472	0.001
205–210	23.652	0.029	16.121	0.027	38.610	0.029	1.632	0.006	1.467	0.029
220–225	23.497	0.035	16.111	0.037	38.669	0.040	1.646	0.008	1.458	0.007
235–240	23.601	0.037	16.113	0.038	38.646	0.038	1.638	0.006	1.465	0.007
250–255	23.636	0.043	16.124	0.042	38.685	0.042	1.637	0.009	1.466	0.008
265–270	23.556	0.034	16.116	0.038	38.699	0.038	1.643	0.007	1.462	0.009
280–285	23.641	0.030	16.124	0.031	38.706	0.031	1.637	0.006	1.466	0.006

Additional evidence on the anthropogenic origin of lead in the Lagoa Vermelha surface sediments will be given by the isotopic study discussed in the following section.

3.3. *Lead isotopes*

The isotopic compositions of lead in sediment samples are listed in Table 1. Although all four isotopic ratios were determined ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$) the discussion will focus on the $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$ ratios which are most commonly used in environmental studies.

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratio profiles show minor fluctuations (1.432–1.494 and 1.589–1.676, respectively) from the base of the sequence up to 30 cm. From 30 cm upwards the $^{208}Pb/^{206}Pb$ ratio increases gradually up to the maximum value of 1.887, while the $^{206}Pb/^{207}Pb$ ratio decreases to 1.278, the lowest value in the entire sediment record. The changes in isotopic composition are mirrored by the Pb EFs which are fairly constant from the base of the core up to 90 cm (average 0.93), increasing slightly from 90 to 30 cm, and thereafter increasing steadily to a maximum value of 3.05 at the surface (Fig. 6A).

The increase of Pb EFs and the concomitant decline of the $^{206}Pb/^{207}Pb$ ratios in the upper 30 cm of the core suggest an influx of exotic lead added to the profile probably through atmospheric deposition. This is because such sources commonly have depleted lead isotopic ratios from those of background geologic materials (Eades et al., 2002).

A $^{206}Pb/^{207}Pb$ against $^{208}Pb/^{206}Pb$ diagram was plotted to provide insight into the potential sources of pollution to the sediments from Lagoa Vermelha (Fig. 6B). Shown are the Pb ratios for all samples of the core, and for possible sources of anthropogenic lead (Table 2). These include emissions originating from the Southern Hemisphere, represented by continental aerosols collected in rural and inner city environments (Bollhöffer and Rosman, 2000), Antarctic snow, recording long-range anthropogenic emissions (Planchon et al., 2003), fuel samples used in Brazil (Gioia et al., 2006), and regional-scale emissions from the Ribeira Valley Lead District (Daitx, 1996).

The Pb isotopic ratios of the Lagoa Vermelha surface sediments (0–30 cm) dispersed along a line, constrained by the isotopic composition of the geogenic background represented by the deepest samples of the core ($^{206}Pb/^{207}Pb$ between 1.548 and 1.594) and the less radiogenic anthropogenic components. In this two

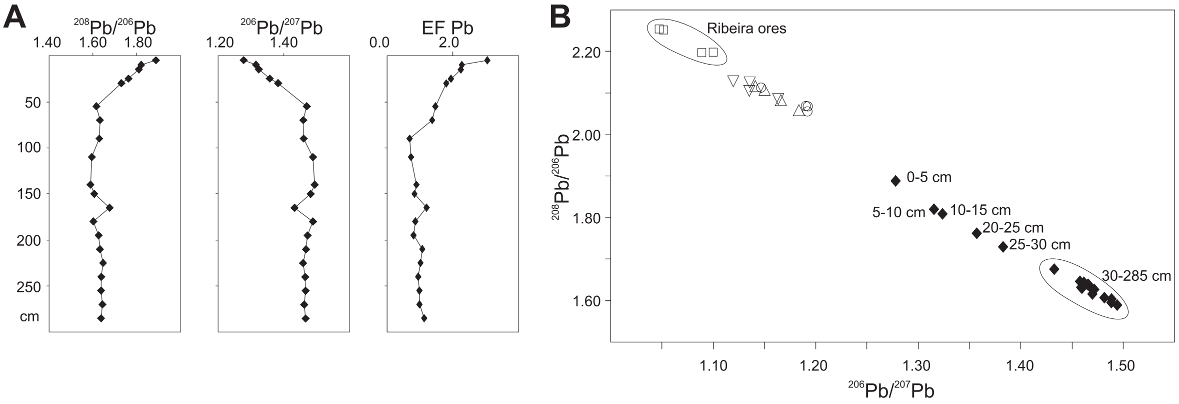

Fig. 6. (A) Pb isotopic ratios ($^{208}Pb/^{206}Pb$, $^{206}Pb/^{207}Pb$), and Pb EFs versus depth; (B) $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ plot, showing the Pb isotopic composition of: ▽ Lagoa Vermelha sediments; ◆ continental aerosols collected in rural and inner city environments throughout the southern hemisphere (Bollhöffer and Rosman, 2000); △ Antartic snow, which records Pb anthropogenic emissions in the southern hemisphere (Planchon et al., 2003); ○ fuel samples used in South American cities (Gioia et al., 2006); □ ores from the Ribeira Valley Mining District (Daitx, 1996).

Table 2
Pb isotope ratios of possible sources of anthropogenic lead.

	References	$Pb^{206/207}$	$Pb^{208/206}$
Continental aerosols collected in rural and inner city environments	Bollhöffer and Rosman (2000)	1.150	2.110
		1.141	2.117
		1.184	2.062
		1.166	2.083
Antarctic snow, recording anthropogenic emissions	Planchon et al. (2003)	1.133	2.108
		1.117	2.132
		1.161	2.089
		1.133	2.126
Fuel samples used in South American cities	Gioia et al. (2006)	1.190	2.069
		1.192	2.056
		1.192	2.068
		1.147	2.114
Orebodies from the Ribeira Valley	Daitx (1996)	1.051	2.252
		1.047	2.255
		1.099	2.199
		1.090	2.200

end-member model, the shift of the isotopic composition toward decreasing radiogenic values in the increasingly younger sediments is consistent with an increasing contribution of airborne anthropogenic lead. However, it is not possible to unequivocally attribute this shift to a particular source. In the uppermost sediments (0–10 cm), the lowest values for the $^{206}Pb/^{207}Pb$ ratios may represent the influence of the less radiogenic Pb from the Ribeira Valley District ores ($^{206}Pb/^{207}Pb$ between 1.04 and 1.10), emitted during the last 50 years.

4. Summary and conclusions

A core representing 2430 ^{14}C years of sediment accumulation was collected from Lagoa Vermelha, a small mountain lake located in the pristine environment of the Upper Ribeira State Park. The Park is situated in the Ribeira Valley, where a Pb–Zn–Ag mining industry was during the second half of the 20th century.

The metal concentrations obtained in the lake sediments are not particularly elevated. However, normalization of concentrations with respect to Sc and calculation of enrichment factors reveal significant increasing trends for Pb, Zn, Hg and Ni in the 0–30 cm sediments, which represent approximately the last 180 years of deposition.

As Lagoa Vermelha is located in a rather isolated area, surrounded by primary vegetation, atmospheric fallout is likely the main pathway by which metals entered the lake ecosystem. The urban and industrial emissions from the industrialized states of southeastern Brazil are the potential sources of metals to the lake. Pb isotopic systematic supports the inference that Pb enrichment in the surface sediments was not linked with a change in natural inputs, but was associated with anthropogenic input. Particularly in respect to the last 50 years, it is likely that exhausts released from processing plants in the Ribeira Valley, enriched in trace metals, were an additional source of metal pollution to the Lagoa Vermelha sediments.

Acknowledgments

The authors are grateful to Abdel Siffedine, IRD, France and Renato C. Cordeiro, Federal Fluminense University, Rio de Janeiro, Brazil, for help with the sampling operation, to Jaime R. Passarini Jr., ^{14}C Laboratory, CENA/USP, for sample preparation for ^{14}C dating, and to two anonymous reviewers for valuable comments on the manuscript. The Brazilian agencies CNPq and FAPESP are acknowledged for financial support.

References

Abbot, M.B., Wolfe, A.P., 2003. Intensive pre-Incan metallurgy recorded by lake sediments from the Bolivian Andes. Science 301, 1893–1895.

Biester, H., Filian, R., Franzen, C., Woda, C., Manzini, A., Schöler, H.F., 2002. Elevated mercury accumulation in a peat bog of the Magellanic Moorlands, Chile (53oS) – An anthropogenic signal from Southern Hemisphere. Earth and Planetary Science Letters 201, 609–620.

Biester, H., Bindler, R., Martinez-Cortizas, A., Engstrom, D.R., 2007. Modeling the past atmospheric deposition of mercury using natural archive. Environmental Science and Technology 41, 4851–4860.

Bollhöffer, A., Rosman, K.J.R., 2000. Isotopic source signatures for atmospheric lead: the Southern Hemisphere. Geochimica et Cosmochimica Acta 64, 3251–3262.

Camarero, L., Botev, I., Muri, G., Psenner, R., Rose, N., Stuchlik, E., 2009. Trace elements in alpine and artic lake sediments as a record of diffuse atmospheric contamination across Europa. Freshwater Biology 54, 2518–2532.

Campanha, G.C., Sadowski, G.R., 1999. Tectonics of the southern portion of the Ribeira Belt (Apiaí Domain). Precambrian Research 98, 31–51.

Cooke, C.A., Abbot, M.B., Wolfe, A.P., Kittelson, J.L., 2007. A millennium of metallurgy recorded by lake sediments from Morococha, Peruvian Andes. Environmental Science and Technology 41, 3469–3474.

Cooke, C.A., Abbot, M.B., Wolfe, A.P., 2008. Late-Holocene atmospheric lead deposition in the Peruvian and Bolivian Andes. The Holocene 18, 353–359.

Cooke, C.A., Balcom, P.H., Biester, H., Wolfe, A.P., 2009a. Over three millennia of mercury pollution in the Peruvian Andes. Proceedings of the National Academy of Sciences 106, 8830–8834.

Cooke, C.A., Wolfe, A.P., Hobbs, W.O., 2009b. Lake-sediment geochemistry reveals 1400 years of evolving extractive metallurgy at Cerro de Pasco, Peruvian Andes. Geology 37, 1019–1022.

Couillard, Y., Cattaneo, A., Gallon, C., Courcelles, M., 2008. Sources and chronology of fifteen elements in sediments of lakes affected by metal deposition in a mining area. Journal of Paleolimnology 40, 97–114.

Dabous, A.A., 2002. Lead-210 geochronology and trace metal geochemistry of sediment cores from Lake overstreet and upper Lake Lafayette, Leon County, Florida. Environmental Geosciences 9, 51–65.

Daitx, E.C., 1996. Origem e evolução dos depósitos sulfetados tipo Perau (Pb–Zb–Ag), com base nas jazidas Canoas e Perau (Vale do Ribeira, PR). Ph.D. thesis. Institute of Geosciences – São Paulo State University/ UNESP, 453 pp. (unpublished).

Eades, L.J., Farmer, J.G., MacKenzie, A.B., Kirika, A., Bailey-Watts, A.E., 2002. Stable lead isotopic characterization of the historical record of environmental lead contamination in dated freshwater lake sediment cores from northern and central Scotland. The Science of the Total Environment 292, 55–67.

El Bilali, L., Rasmussen, P.E., Hall, G.E.M., Fortin, D., 2002. Role of sediment composition in trace metal distribution in lake sediments. Applied Geochemistry 17, 1171–1181.

Gioia, S.M.C.L., Pimentel, M.M., Tessler, M., Dantas, E.L., Campos, J.E.G., Guimarães, E.M., Maruoka, M.T.S., Nascimento, E.L.C., 2006. Sources of anthropogenic lead in sediments from an artificial lake in Brasilia, central Brazil. The Science of the Total Environment 356, 125–142.

Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. Journal of Paleolimnology 25, 101–110.

Hosono, T., Su, C.-C., Okamura, K., Taniguchi, M., 2010. Historical record of heavy metal pollution deduced by lead isotope ratios in core sediments from the Osaka Bay, Japan. Journal of Geochemical Exploration 107, 1–8.

Karageorgis, A.P., Katsanevakis, S., Kaberi, H., 2009. Use of enrichment factors for the assessment of heavy metal contamination in the sediments of Koumoundourou Lake, Greece. Water, Air and Soil Pollution 204, 243–258.

Karmann, I., Cruz Jr., F.W., Viana Jr., O., Burns, S.J., 2007. Climate influence on geochemistry parameters of waters from Santana-Pérolas cave system. Brazil. Chemical Geology 244, 232–247.

Lacerda, L.D., Ribeiro, M.G., 2004. Changes in lead and mercury atmospheric deposition due to industrial emissions in southeastern Brazil. Journal of the Brazilian Chemical Society 15 (6), 931–937.

Lepane, V., Varvas, M., Viitak, A., Alliksaar, T., Heinsalu, A., 2007. Sedimentary record of heavy metals in Lake Liinjärv, southern Estonia. Estonian Journal of Earth Sciences 56, 221–232.

Li, Y.-H., Takamatsu, T., Sohrin, Y., 2007. Geochemistry of Lake Biwa revisited. Limnology 8, 321–330.

Mahler, B.J., Van Metre, P.C., Callender, E., 2006. Trends in metals in urban and reference lake sediments across the United States, 1970 to 2001. Environmental Toxicology and Chemistry 25, 1698–1709.

Martin, M., Flexor, J.M., Suguio, K., 1995. Vibrotestemunhador leve: construção, utilização e potencialidades. Boletim do Instituto de Geociências da Universidade de São Paulo 16, 59–66.

Michellutti, N., Simonetti, A., Briner, J.P., Funder, S., Creaser, R.A., Wolfe, A.P., 2009. Temporal trends of pollution Pb and other metals in east-central Baffin Island inferred from lake sediment geochemistry. The Science of the Total Environment 407, 5653–5662.

Moraes, R.P., Figueiredo, B.R., Lafon, J.-M., 2004. Pb-isotopic tracing of metal pollution sources in the Ribeira Valley, southeastern Brazil. Terrae 1, 26–33.

Nascimento, F.S., do, Losno, R., Colin, J.L., Mello, W.Z., de, Silva, H.E.da, 2011. Atmospheric total suspended particulate trace element identification by XRF at

Ilha Grande, State of Rio de Janeiro, Brazil. Water, Air, and Soil Pollution 214, 525–538.

Ng, S.L., King, R.H., 2004. Geochemistry of lake sediments as a record of environmental changes in a High Artic watershed. Chemie der Erde 64, 257–275.

Nriagu, J.O., 1990. Global metal pollution. Poisoning the biosphere? Environment 32, 7–31.

Nriagu, J.O., 1996. A history of global metal pollution. Science 272, 223–224.

Nriagu, J.O., Jinabhai, C., Naidoo, R., Coutsoudis, A., 1996. Atmospheric lead pollution in KwaZulu/Natal, South Africa. The Science of the Total Environment 191, 68–76.

Outridge, P.M., Hermanson, M.H., Lockhart, W., 2002. Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Artic. Geochimica et Cosmochimica Acta 66, 3521–3531.

Outridge, P.M., Stern, G.A., Hamilton, P.B., Percival, J.B., McNeely, R., Lockhart, W.L., 2005. Trace metal profiles in varved sediment of an Artic lake. Geochimica et Cosmochimica Acta 69, 4881–4894.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environmental Reviews 9, 269–298.

Pearson, L.K., Hendy, C.H., Hamilton, D.P., Pickett, R.C., 2010. Natural and anthropogenic lead in sediments of the Rotorua lakes, New Zealand. Earth and Science Planetary Letters 297, 536–544.

Perry, E., Norton, S.A., Kamman, N.C., Lorey, P.M., Driscoll, C.T., 2005. Deconstruction of historic mercury accumulation in lake sediments, Northeastern United States. Ecotoxicology 14, 85–89.

Planchon, F.A.M., Velde, K.V., de, Rosman, K.J.R., Wolff, E.W., Ferrari, C.P., Boutron, C.F., 2003. One hundred fifty-year record of lead isotopes in Antarctic snow from Coats Land. Geochimica et Cosmochimica Acta 67, 693–708.

Planchon, F.A.M., Boutron, C.F., Barbante, C., Cozzi, G., Gaspari, V., Wolff, E.W., Ferrari, C.P., Cescon, P., 2002. Changes in heavy metals in Antartic snow from Coats land since the mid-19th to the late 20th century. Earth and Planetary Science Letters 200, 207–222.

Reimann, C., Arnoldussen, A., Englmaire, P., Filtzmoser, P., Finne, T.E., Garret, R.G., Koller, F., Nordgullen, O., 2007. Element concentrations and variations along a 120-km transect in southern Norway - anthropogenic vs. geogenic vs. biogenic element sources and cycles. Applied Geochemistry 22, 851–871.

Renberg, I., Brannvall, M.L., Bindler, R., Emteryd, O., 2002. Stable lead isotopes and lake sediments – a useful combination for the study of atmospheric lead pollution history. The Science of the Total Environment 292, 45–54.

Roos-Barraclough, F., Martinez-Cortizas, A., Garcia-Rodeja, E., Shotyk, W., 2002. A 14,500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation. Earth and Planetary Science Letters 202, 435–451.

Rosman, K.J.R., Chisholm, W., Hong, S., Candelone, J.-P., Boutron, C.F., 1997. Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 BC to 300 AD. Environmental Science and Technology 31, 3413–3416.

Shotyk, W., Weiss, D., Kramer, J.D., Frei, R., Cheburkin, A.K., Gloor, M., Reese, S., 2001. Geochemistry of the peat bog at Etang de la Gruyère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 ^{14}C yr BP. Geochimica et Cosmochimica Acta 65, 2337–2360.

Shotyk, W., Goodsite, M.E., Roos-Barraclough, F., Givelet, N., Le Roux, G., Weiss, D., Cheburkin, A.K., Knudsen, K., Heinemeir, J., der Kanaap, W.O., van NortonLohose, S.A., Lohose, C., 2005. Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe islands. Geochimica et Cosmochimica Acta 69, 1–17.

Shuchun, Y., Bin, X., Weilan, X., Yuxing, Z., Shijie, L., 2009. Lead pollution recorded in sediments of three lakes located at the middle and lower Yangtze River basin, China. Quaternary International 208, 145–150.

Silva-Filho, E.V., Wasserman, J.C., Lacerda, L.D., 1998. History of metals inputs recorded on sediment cores from a remote environment. Journal of the Brazilian Association for the Advancement of Science 50 (5), 374–376.

Silva-Filho, E.V., Machado, W., Oliveira, R.R., Sella, S.M., Lacerda, L.D., 2006. Mercury deposition through litterfall in an Atlantic Forest at Ilha Grande, Southeast Brazil. Chemosphere 65, 2477–2484.

Soil Survey Staff. United States Department of Agriculture, 1999, Second ed. Soil Taxonomy: a Basic System of Soil Classification for Making and Interpreting Soil Surveys, vol. 869. USDA, Washington (Agriculture Handbook, 436).

Van der Velde, K., Barbante, C., Cozzi, G., Moret, I., Bellomi, T., Ferrari, C., Boutron, C., 2000. Changes in the occurrence of silver, gold platinum, palladium and rhodium in Mont Blanc ice and snow since the 18th century. Atmospheric Environment 34, 3117–3127.

Von Gunten, H.R., Sturm, M., Moser, R.N., 1997. 200-year record of metals in lake sediments and natural background concentrations. Environmental Science and Technology 31, 2193–2197.

Wang, X., Yang, H., Gong, P., Zhao, X., Wu, G., Turner, S., Yao, T., 2010. One century sedimentary records of polycyclic aromatic hydrocarbons, mercury and trace elements in the Qinghai Lake, Tibetan Plateau. Environmental Pollution 158, 3065–3070.

Weiss, D., Shotyk, W., Appleby, P.G., Kramers, J.D., Cheburkin, A.K., 1999. Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. Environmental Science and Technology 33, 1340–1352.

Woodhead, J.D., Hergt, J.M., 1999. Pb-isotope analyses on USGS Reference Material. Geostandards Newsletter 24 (1), 33–38.

Wu, Y., Hou, X., Cheng, X., Yao, S., Xia, W., Wang, S., 2007. Combining geochemical and statistical methods to distinguish anthropogenic sources of metals in lacustrine sediments: a case study in Dongjiu Lake, Taihu Lake catchment, China. Environmental Geology 52, 1467–1474.

Yang, Z.R., Graham, E.Y., Lyons, W.B., 2003. Geochemistry of Pyramid lake sediments: influence of anthropogenic activities and climatic variations within the basin. Environmental Geology 43, 688–697.

Yang, H., Battabee, R.W., Turner, S.D., Rose, N.L., Derwent, R.G., Wu, G., Yang, R., 2010. Historical reconstruction of mercury pollution across the Tibetan Plateau using lake sediments. Environmental Science and Technology 44, 2918–2924.